STUDIES OF SPECTRAL BEHAVIOUR OF COPPER(II) COMPLEXES OF AROMATIC SCHIFF BASES AND OF SECONDARY AMINES

By

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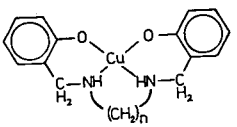
A series of amines of the type $C_6H_4(OH).CH_2.NH.(CH_2)_n.NH.CH_2.C_6H_4(OH)$ (n = 2—7 9, 10) were prepared by $NaBH_4$ reduction of salicylidene anilines, and their copper(II) complexes too were prepared. From the results of u.v., i.r. spectral and magnetic moment investigations it is probable that these secondary amines form monomeric, square-planar CuL-type chelate complexes with Cu(II) ions.

Compounds of bivalent copper are known to exhibit different coordination states, some being four-coordinate, whereas others are five-, or occasionally six-coordinate; a weaker ligand field generally leads to an increased coordination number [1]. In an earlier paper [2] we described the spectra of secondary amines obtained by $NaBH_4$ reduction of salicylidene anilines and also the spectra of their copper(II) complexes. As an extension of this work we have prepared a series of amines of type $C_6H_4(OH).CH_2.NH(CH_2)_nNH.CH_2.C_6H_4(OH)$ (Structure 1) (n=2−7, 9, 10), in



a similar way as previously, together with their copper chelates. In the present paper we report on the u.v. and visible spectral behaviour of these compounds, and compare the spectra of some copper chelates of the corresponding tetradentate parent Schiff bases (n=2, 4, 6, 10) with those of their adducts with phenol derivatives.

Experimental

Preparation of amines.

A two-fold molar amount of $NaBH_4$ was added in portions to a methanolic solution of the Schiff base, and the mixture was refluxed for fifteen minutes. The amines were liberated from the colourless solutions on addition of distilled water; the products were recrystallized from aqueous ethanol. All the amines prepared are white solids, practically insoluble in water, but readily soluble in organic solvents. The analytical data are listed in Table I.

Table I

Analytical data on secondary amines and their copper(II) complexes

n	C%		H%		M. p.*	C%		Cu%	
	Calcd.	Found	Calcd.	Found		Calcd.	Found	Calcd.	Found
2	70.56	70.48	7.40	7.34	121.5—121.7	57.56	57.65	19.03	18.80
3	71.30	71.22	7.74	7.78	107.2—107.4	58.69	58.56	18.26	18.09
4	71.97	71.96	8.05	8.00	119.5—119.8	59.73	59.48	17.56	17.44
5	72.58	72.51	8.33	8.31	98.5—98.7	60.70	60.65	16.90	16.80
6	73.13	73.09	8.59	8.48	110.6—110.8	61.59	61.70	16.29	16.11
7	73.64	73.60	8.83	8.75	98.0—98.8	62.43	62.49	15.73	15.60
9	74.55	74.55	9.25	9.27	99.5—99.7	63.94	63.70	14.71	14.62
10	74.96	74.29	9.44	9.40	106.7—106.9	64.62	64.56	14.24	14.09

* Uncorrected values.

Preparation of copper(II) chelates.

To a mixture of a warm aqueous solution of copper(II) acetate monohydrate (0.01 mole) and a slight excess of secondary amine in methanol, was added 0.01 mole NaOH in water. From the green solutions, crystalline products separated out immediately or after 24 hours. The products were filtered off, and washed with ethanol and ether. The complexes are deepgreen; they are soluble in polar organic solvents, but their solubility decreases as the length of the methylene chains increases. The analytical data are given in Table I.

Preparation of adducts.

A mixture of CuBHSAL-en* and the corresponding phenol derivative in 1:1 mole ratio was warmed above the m.p. of the phenol component; immediate formation of a violet addition compound occured. The mass was washed with chloroform or chloroform-benzene to remove the excess of phenol. The analytical data prove the formation of 1:1 adducts.

* N,N-ethylenebis(salicylaldimine)copper(II)

Spectral measurements.

The u.v. and visible spectra were measured at 295 K on a SPECORD UV—VIS spectrofotometer, using spectrograde solvents. The reflection spectra were measured without dilution, against a MgO standard on a BECKMAN DU spectrophotometer, in KBr discs and in chloroform solution.

Results and Discussion

U.v. spectra of secondary amines.

The spectral data on the secondary amines studied are presented in Table II; typical spectra are shown in Fig. 1.

Table II

U.v. spectral data on secondary amines in different media

n=	Solvent*	nm and log ε	n=	Solvent*	nm and log ε
2	M	205(4.18) ~218 274(3.59)	6	M	206(4.33) ~215 277(3.74)
	A	203(4.18) 216(4.08) 278(3.73)		A	202(4.21) 217(4.05) 276(3.63)
	B	213(4.25) 241(4.20) 293(3.85)		B	212(4.32) 241(4.27) 293(3.80)
3	M	207(4.20) ~216 277(3.64)	7	M	203(4.32) ~218 277(3.48)
	A	203(4.22) 216(4.15) 276(3.80)		A	202(4.23) 216(4.11) 276(3.67)
	B	212(4.29) 241(4.15) 293(3.79)		B	212(4.30) 241(4.15) 294(3.71)
4	M	206(4.27) ~215 276(3.69)	9	M	203(4.33) ~218 277(3.64)
	A	202(4.21) 216(4.08) 277(3.73)		A	202(4.29) 216(4.13) 277(3.79)
	B	212(4.32) 241(4.21) 293(3.85)		B	211(4.43) 241(4.29) 292(3.93)
5	M	203(4.27) ~218 277(3.59)	10	M	203(4.35) ~218 278(3.56)
	A	202(4.25) 216(4.16) 276(3.82)		A	202(4.28) 216(4.06) 277(3.73)
	B	211(4.33) 241(4.18) 293(3.81)		B	211(4.38) 241(4.21) 293(3.84)

* M: methanol; A: 0.1 mol dm^{-3} H_2SO_4/CH_3OH; B: 0.1 mol dm^{-3} $NaOH/CH_3OH$

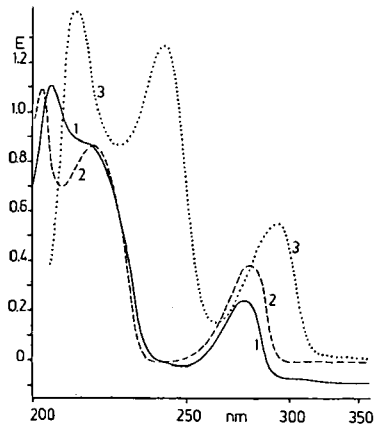


Fig. 1. U. v. spectra of N,N'-ethylenebis(o-hydroxybenzylamine). **1**: in methanol, $c = 7.7.10^{-4}$ mol/dm^3; **2**: in 0.1 H_2SO_4/CH_3OH, $c = 7.3.10^{-4}$ mol/dm^3; **3**: in 0,1 $NaOH/CH_3OH$, $c = 8.1.10^{-4}$ mol/dm^3. d = 0.1 cm; T = 295 K

The structures of the u.v. spectra of the amines are completely similar. The methanolic solutions show two characteristic bands, at 202—206 and 274—278 nm, with a shoulder at about 218 nm; the bands are interpreted as $\pi^* \leftarrow \pi$ bands. The intensity of the first band increases with increasing methylene chain length. In acidic solution a band appears at 216—218 nm, too; we assumed that this band corresponds to the protonated form of the amine molecule. In basic media the band intensities increase and the maxima show a red shift. It is interesting that the energy of the bands shows no dependency on n, but the intensity is higher for odd n.

Visible spectra of copper chelates.

The relevant features of the solution spectra of the complexes studied are summarized in Table III; a typical set of curves is given in Fig. 2.

The reflection spectra of copper(II) chelates are characteristic of square-planar complexes; a band is found in the range 600—650 nm. It may be noted that a plot of λ_{max} *vs.* the number of carbon atoms in the alkyl chain is zigzag in shape; λ_{max} is generally higher for an odd number of C atoms. In chloroform solution a medium-intensity and a flat band ($\varepsilon \sim 700$—1600) appear at about 660—580 and 380—420 nm, respectively. Dissolution of green CuBHSAL-en in chloroform or in glacial acetic acid results in a purple solution; the phenomena were interpreted by adduct formation [3, 4]. A similar colour change is not observed for the complexes of secondary amines. There is a marked spectral difference between the two types of complexes having bands of significantly higher intensity ($\varepsilon \sim 8000 - 12\,000$) in the region 380—420 nm.

WATERS et al. [5, 6] proposed that the green copper complexes possess an effective coordination number exceeding four, due either to intermolecular association or to adduct formation with LEWIS bases, while the brown or violet complexes contain four-coordinate copper(II). The green complexes generally absorb less in the 500 nm region and more in the 700 nm region than do the brown or violet complexes.

For copper(II) ions, theory predicts that three or four transitions should occur within the 3d orbitals, depending on the symmetry involved [7, 8]. In most cases the spectra of planar copper(II) complexes display only a single band, making assignment of individual electronic transitions difficult. The CD spectra of optically active copper(II) complexes indicate the presence of three transitions [7]; these have been

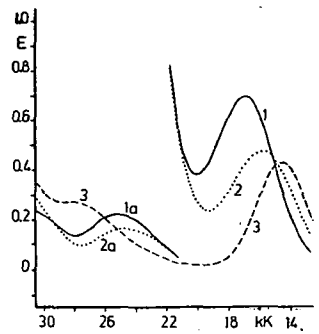


Fig. 2. Visible spectra of N,N'-ethylenebis(o-hydroxybenzylamine)copper(II). **1**: in chloroform, $c = 2.2.10^{-3}$ mol/dm³; **2**; in pyridine, $c = 2.1.10^{-3}$ mol/dm³; **3**: in glacial acetic acid, $c = 2.4.10^{-3}$ mol/dm³. d=for 1, 2, 3: 1.0 cm, for **1a**, **2a**: 0.1 cm,: t=295 K

Table III

Visible spectral data on copper(II) chelates of secondary amines and of Schiff bases

n=	Solvent a)	nm and ε			
		Chelates of sec. amines		Chelates of Schiff bases	
2	Chl.	595(325)	396(1150)	573(380)	371(10 965)
	Py	638(235)	406(810)	601(282)	369(10 720)
	HAc	683(190)	~358	568(365)	351(9 120)
3	Chl.	658(130)	396(1100)		
	Py	611(225)	401(815)		
	HAc	683(248)	~370		
4	Chl.	b)		644[c]	382[c]
	Py	635(180)	~385	661[c]	382[c]
	HAc	687(186)	~365	687(148)	357(8 710)
5	Chl.	~625	420(730)		
	Py	661(178)	408(863)		
	HAc	687(195)	~358		
6	Chl.	~618	433(1230)	~617	399(9 550)
	Py	641(225)	414(975)	613(167)	368(9 330)
	HAc	683(218)	~365	683(177)	357(7 908)
7	Chl.	~625	420(1410)		
	Py	668(163)	388(870)		
	HAc	676(220)	347(226)		
9	Chl.	~628	417(1462)		
	Py	672(164)	391(900)		
	HAc	691(196)	353(265)		
10	Chl.	~632	395(1088)	~617	368(11 750)
	Py	676(175)	~385	625(130)	365(11 220)
	HAc	687(205)	352(196)	687(182)	355(9 120)

[a] Chl.: chloroform; Py: pyridine; HAc: glacial acetic acid;
[b] Very low solubility; [c] Saturated solution at room temperature.

assigned to $d_{z^2} \leftarrow d_{xy}$, $d_{x^2-y^2} \leftarrow d_{xy}$ and probably $d_{xz} \leftarrow d_{xy}$ in the sequence of increasing energy under C_2 symmetry.

The spectra of the complexes recorded in Table III show a pronounced absorption in the 580—660 nm region; this band can be assigned as a d—d band. The *cis*-acentric copper(II) chelates generally have d—d-bands of higher intensity than those of the related *trans* chelates [9]. Our results show that the chelates of secondary amines have bands with intensities of $\varepsilon \sim 150$—350, so the possibility of a polymeric structure is not excluded. CuBHSAL-en, containing *cis*-planar moieties, has a band of higher intensity ($\varepsilon = 380$) in this region (Fig. 3).

Interpretation of the medium-intensity band found in the range 380—420 nm for chelates of secondary amines is difficult. According to YAMADA et al. [10], this band is closely related to a copper-copper interaction, but on the basis of our experimental data it may only be stated that the 380—420 and 580—660 nm bands are of completely different origins.

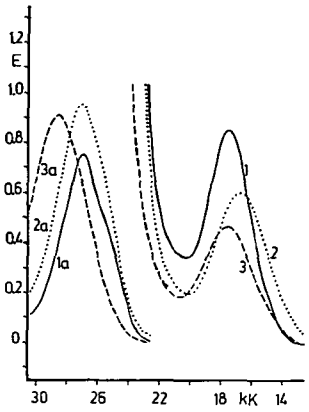


Fig. 3. Visible spectra of N,N'-ethylenebis(salicylidene-iminato) copper(II). **1**: *in* chloroform, $c = 2.2.10^{-3}$ mol/dm³; **2**: *in* pyridine, $c = 2.1.\ 10^{-3}$ mol/dm³; **3**: in glacial acetic acid, $c = 2.4.10^{-3}$ mol/dm³; d = for 1—3: 1.0 cm; curves **1a**—**3a** are illustrated with an arbitrary scale

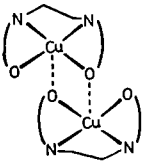
In pyridine the bands are shifted by ca. 20—50 nm towards lower energy, and the spectra of the products crystallized from pyridine are the same as those of the original compounds. The experimental results demonstrate that no adduct formation takes place, similarly as for CuBHSAL-en [11]. In glacial acetic acid the bands are shifted further to lower energy. In N-bases (pyridine, 2- and 4-picoline, 2,4,6-collidine) the two groups of chelates behave similarly; with increase in pK the visible bands shift to higher energy and their intensities increase, too.

The magnetic measurements of LEWIS and WALTON [11] indicate that there is no significant exchange interaction between the copper atoms in the case of CuBHSAL-en. The copper(II) derivatives of tetradentate ligands of BHSAL-en type exhibit a decrease in ligand field strength as the number of CH_2 groups increases; this decrease is coupled with a small increase in magnetic moment [12]: BM for $n = 2$: 1.84, $n = 3$: 1.89, $n = 4$: 1.94. This change is interpreted as being indicative of an increasing distortion from planarity towards tetrahedral geometry [12]. CuBHSAL-hxmda* is an exception (BM = 1.74 [12]; its structure is probably polymeric, as can be seen in Structure 3 [13]. Our preliminary magnetic measurements show that the magnetic moments of chelates of secondary amines fall in the range 1.85—2.05 BM, and no relation can be found between the BM values and the chain length. These values probably correspond to a square-planar arrangement, and they indicate no magnetic interaction between the atoms, if we assume a polymeric structure.

There are important differences between the i.r. spectra of the complexes of the two types. The NH strething frequency can be found at around 3100 cm^{-1}, its position being almost independent of the alkyl chain length. Several frequencies are absorbed in the interval 1200—1600 cm^{-1}, corresponding to vibrations of the aromatic systems. We assigned the 1270—1280 cm^{-1} band to the $\nu C-O$ vibration. On the basis of the i.r. spectra the coordination of acetate ion can be excluded, in contrast with the aniline derivatives discussed earlier [2].

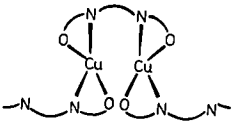
* N,N'-hexamethylenediaminebis(salicylaldimine) copper(II)

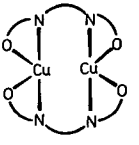
X-ray determinations [14, 15] have shown that CuBHSAL-en is dimeric (Structure 2), with copper-to-oxygen bridges joining the two units of the dimer, in which



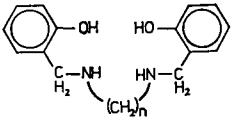
the copper(II) ions are in an essentially square-pyramidal environment. A basically similar structure is found [16] for the trimethylene-bridged analogue, too. Unfortunately, there is no structural information on chelates of secondary amines, so we can present only suppositions in connection with the stereochemical arrangement.

Besides the experimental results already discussed the following must also be taken into account. In one respect, an additional methylene group would allow the donor atoms to move out of square-planar coordination positions. On the other hand, with increasing length of the polymethylene chain there would be an increasing tendency for the potentially tetradentate ligand to bind two copper(II) ions, each in a bidentate fashion (Structures 3, 4).





On the basis of the data available in this study it is not possible to determine unambiguously the stereochemistry of these chelates. We consider it most likely that monomeric square-planar molecules are formed (at least in solution), independently of the length of the methylene chains (Structure 5). The results of osmometric measurements also suggest monomeric species.



*Comparison of spectral and other behaviour of CuBHSAL-en and CuBEBA.** The spectral data measured in different organic solvents are listed in Table IV. The long-wave band of CuBHSAL-en appears at 560—600 nm ($\varepsilon \sim 320-450$) and no correlation can be found between λ_{max} and the dielectric constants ε; however, a plot of λ_{max} *vs.* the donor number DN [17, 18] gives a linear relationship. The 350—360 nm band has a very high intensity, $\varepsilon \sim 9000$—12 000. The visible band of CuBEBA is shifted by ca. 10—40 nm to lower energy ($\varepsilon \sim 150$—300); the λ_{max} *vs.*

* N,N'-ethylenebis(o-hydroxybenzylamine) copper(II)

Table IV

Spectral data on CuBHSAL-en and CuBEBA in different solvents

Solvents	ε	λ/nm of bands			
		Chelates of Schiff bases		Chelates of sec. amines	
DMSO	46.68	580	365	618	392
Acetonitrile	37.50	573	362	604	392
DMFA	36.71	578	365	612	395
Nitromethane	35.87	570	364	586	394
Nitrobenzene	34.80	571	—	594	—
Acetone	20.70	575	366	607	395
Pyridine	12.40	601	369	641	407
MeOH	32.70	565	356	592	391
EtOH	24.55	568	360	583	394
n-PrOH	20.33	568	362	586	395
CH_2Cl_2	8.93	573	368	591	399
$CHCl_3$	4.806	573	371	597	397
Benzene	2.275	574	374	590	404
Cl-Benzene		578	374	595	395
p-Xylene	2.2699	586	373	insol.	
Dioxane	2.209	587	370	599	398
Glac. ac. acid	6.15	568	351	688	~360

DN plot also gives a straight line. The 380—400 nm band has a lower intensity ($\varepsilon \sim 800$—2000) than that for CuBHSAL-en.

One marked difference between the two complexes is that CuBHSAL-en reacts with metal halides or perchlorates to form bi- and trinuclear complexes [12, 19, 20], while for CuBEBA this is not observed.

TANAKA [4] has reported that CuBHSAL-en forms an adduct with general formula CuBHSAL-en.B with chloroform, glacial acetic acid and phenol derivatives. X-ray determinations have shown [5] that these adducts are monomeric, four-coordinate and essentially planar; the above molecules are bound to the oxygen donor atoms and not to the metal [16, 21]. We have prepared and investigated a series of CuBHSAL-en. n-X-phenol-type adducts (n-X: H, 2-CH_3, 2-Cl, 2-OH, 2-NO_2, 4-CH_3, 4-Cl, 4-OH, 4-NO_2). With the exception of the 2-NO_2-phenol derivative (green) all the adducts are violet solids soluble in chloroform. Their reflection spectra show a broad band at about 560—580 nm, while in chloroform two bands are found, at 560—570 and 360—370 nm, respectively. The substituents X have no significant effect on the band positions. Similar adduct formation was not observed for any chelate of secondary amines.

Our further detailed investigations are in progress.

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ИЗУЧЕНИЕ СПЕКТРОСКОПИЧЕСКИХ СВОЙСТВ КОМПЛЕКСОВ МЕДИ (II) С АРОМАТИЧЕСКИМИ ОСНОВАНИЯМИ ШИФА И ВТОРИЧНЫМИ АМИНАМИ

Й. Часар

Натрий боргидридным восстановлением салицилидене-анилинов синтезирована серия аминов типа $C_6H_4(OH)CH_2NH(CH_2)NHCH_2C_6H_4$ (OH)(n=2–7, 9–10) и их комплекса с медью(II). На основании УФ- и ИК-спектроскопии и данных по магнитным моментам соединений можно предположить, что эти вторичные амины образуют плоские квадратные хелатные комплексы типа CuL с ионами меди (II).